Characterization of silver polyaniline nanocomposite thin films prepared by microwave induced plasma

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Abstract

Polyaniline (PANI) and Ag/PANI nanocomposite thin films have prepared by microwave induced plasma. The Ag powder of average particle size of 50 nm, were used to prepare Ag/PANI nanocomposite thin films. The Ag/PANI nanocomposite thin films prepared by polymerization in plasma and characterized by UV-VIS, FTIR, AFM and SEM to study the effect of silver nanoparticles on the optical properties, morphology and structure of the thin films. The optical properties studies showed that the energy band gap of the Ag/PANI (5%wt silver) decreased from 3.6 to 3.2 eV, where the substrate location varied from 4.4 to 3.4 cm from the axis of the cylindrical plasma chamber. Also the optical energy gap decreased systematically from 3.3 to 3 eV with increasing Ag nanoparticles, where Ag concentration increased from 5% to 11%wt. The FTIR measurement showed a shifting in the FTIR absorption peaks with Ag concentration. AFM and SEM images indicate that there are a few clusters of Ag and there is a uniform distribution of the Ag nanoparticles in the PANI matrix. It can be concluded that Ag/PANI nanocomposite thin films with controlled optical energy band gap can be prepared by microwave induced plasma technique.

Key words

plasma polymerization, polyaniline nanocomposite, microwave induced plasma.

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توصيف اغشية متراكبات متعدد الانيلين فضة النانوية الرقيقة المحضرة بالبلازما المحتثة بالامواج المايكروية

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الخلاصة

حضرت أغشية رقيقة للبولي أنيلين (PANI) و لمتراكب Ag/PANI بطريقة البلازما المحتثة بالمايكروويف. وكان معدل حجم مسحوق الفضة المستخدم 50 نانومتر. حضر المتراكب Ag/PANI بطريقة البلمرة بالبلازما وتم توصيف الأغشية الرقيقة الناتجة بوساطة UV-Vis, FTIR, AFM, SEM لدراسة تأثير الفضة على الخواص البصرية وشكل سطوح وتركيب الأغشية الرقيقة . دراسة الخواص البصرية بينت إن فجوة الطاقة للمتراكب Ag/PANI وبتركيز 5% نسبة وزنيه من الفضة قلت من 3.6- 3.2 إلكترون فولت، حيث أن موقع أرضية الترسيب تغير من 4.4 - 3.4 سم عن محور البلازما. أيضا فجوة الطاقة قلت من 3.3 - 3 إلكترون فولت مع زيادة تركيز جسيمات الفضة من 5% إلى 11% نسبه وزنيه. قياس الطيف للغشاء الرقيق بالأشعة تحت الحمراء بين إن هناك إزاحة في قمة الامتصاص مع إضافة جسيمات الفضه . صور AFM و SEM تشير إلى وجود تجمعات قليلة من جسيمات الفضة مع توزيع منتظم للجسيمات النانوية . ومن الممكن استنتاج إن هناك إمكانية السيطرة على فجوة الطاقة للأغشية الرقيقة للمتراكب النانوي Ag/PANI المحضرة بطريقة البلازما المحتثة بالمايكروويف.

Introduction

Using inorganic polymer metallic nanocomposite can provide high-performance novel materials that find applications in many industrial fields[1]. After Au was first used as an inorganic nano filler in polymer inorganic nanocomposite for optical applications, other metals such as Ag, Cu and Hg were also used with natural polymers for similar optical applications [2]. The nanocomposites of metal and semiconductor particles are important in several optical and electronic applications [3]. The conducting polyaniline (PANI) is one of the promising conducting polymers due to its high conductivity, ease preparation, good environmental stability and large variety of applications which make this polymer suitable as a matrix for preparation of conducting polymer nanocomposites [4]. Polymers are usually polyconjugated structures which are insulators in their pure state; but when treated with oxidizing or reducing agents they can be converted into polymer having reasonable electrical conductivity[5]. In a polymer, the σ and the π-bonded systems lead to the conduction in a π conjugated polymer, the bond between adjacent carbon atoms alternate between single and double bonds[2][4]. In 1950 Rudolf Peierls found that it is energetically favorable for such a chain to distort spontaneously, creating a gap between the filled valance and the unfilled conduction band and converting a chain from a conductor to a semiconductor [6]. The reason for the wide application range of high frequency (HF) plasmas that they have good power efficiency. In a direct current plasma the charges are always accelerated to the opposite electrode and are eventually lost there. In an oscillating field with an alternating polarization, it is clear that it is possible to contain charges for a much longer time. Moreover, high frequency plasma can be electrode contact-free. The latter is essential for high-purity deposition systems, because no sputtering products from the electrodes are present in the process plasma [7].

In this work nanocomposite thin films of polyaniline with silver nanoparticles were deposited on glass substrates by plasma polymerization of aniline.

Experimental set-up

The microwave plasma system consisted of cylindrical stainless steel vacuum chamber of 10 cm inner diameter and 30 cm length. The cylindrical chamber have many ports, one port was coupled with double stage rotary vane vacuum pump, pumping speed of $8m^3/h$ from L.H., to maintain a vacuum of about 10^{-2} mbar. The other port was used to introduce the sample (aniline with Ag nanoparticles) which was injected to the plasma chamber using electrical car injector nozzle. The quantity of the injected liquid can be controlled by special electrical circuit that controlling the injector output. Also, there was a view window that fixed at the side port.

The two ends port of the cylindrical chamber were closed with two flanges that have a circular holes at their centers and there was quartz glass tube passing through these two holes along the cylindrical chamber axis. The inside of the tube is at atmospheric pressure whereas the outside is at low pressure. All these parts were assembled with o-rings joined them to maintain the vacuum in the chamber. After proper evacuation time, Argon was fed to the chamber, as a working plasma gas, through a needle valve to control the gas flow precisely. The filling pressure in the chamber was monitored using Pirani gauge. To avoid the heat that was generated by

the plasma in the chamber, air blower cooling was fixed at the other end of the quartz pipe. The microwave was generated by means of 750 watt magnetron working at frequency of 2.45GHz.

The microwave output from the magnetron was transmitted through a rectangular waveguide which hold a TE_{10} transmission mode. A copper pipe of diameter (8 mm) was inserted at one ends of the glass tube through the waveguide at a certain position that represented a maximum of the standard wave oscillating in the waveguide, this copper pipe working as antenna that transmitting the microwave radiation from the waveguide to the vacuum chamber when passing through the quartz tube along its axis. In fact this configuration can be considered as a coaxial cable transmission line where the copper pipe represents the central conductor of the cable, while the glass tube represents its outer insulator and the generated plasma which is a conductive medium replaces the missing outer conductor of the coaxial cable. When the electric field strength, that transmitted through the copper antenna, exceeds the breakdown field strength the discharge ignites in the outer low pressure regime concentrated at the ends of the glass tube. Within increasing microwave power the plasma grows along the tube and axially homogeneous plasma is formed, the space occupied by the plasma is proportional to many factors such as microwave power and working gas pressure. The glass substrate after good cleaning, were fixed at certain positions just below the plasma, as we avoid putting the substrate within the plasma directly because the polymer films burned at this position. The nanocomposite polyaniline thin films were deposited on the glass substrates by using different concentrations of silver nanoparticles of (5%,7% and 11%wt.) with aniline.

The thickness of the deposited films depended on the quantity of the injected mixture. It was injected in the Ar plasma as pulses of controlled duration. This control of pulse duration and number of pulses was necessary to keep the pressure in the chamber within certain range, that was (0.5-2.0 mbar) which is of great importance to maintain the plasma working.

The schematic diagram and a photograph of the experimental arrangement is shown in Fig. 1 and 2 respectively.

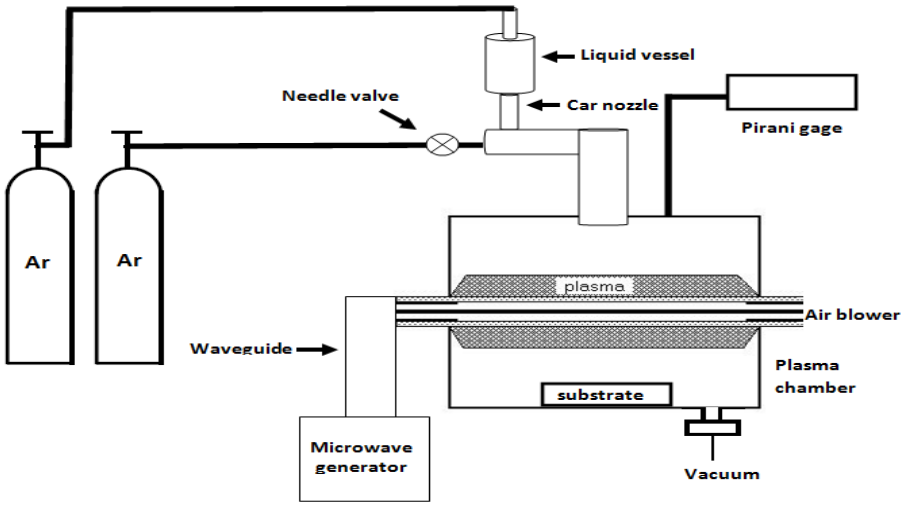


Fig. 1: Schematic diagram for microwave induced plasma system for nanocomposite thin films deposition.

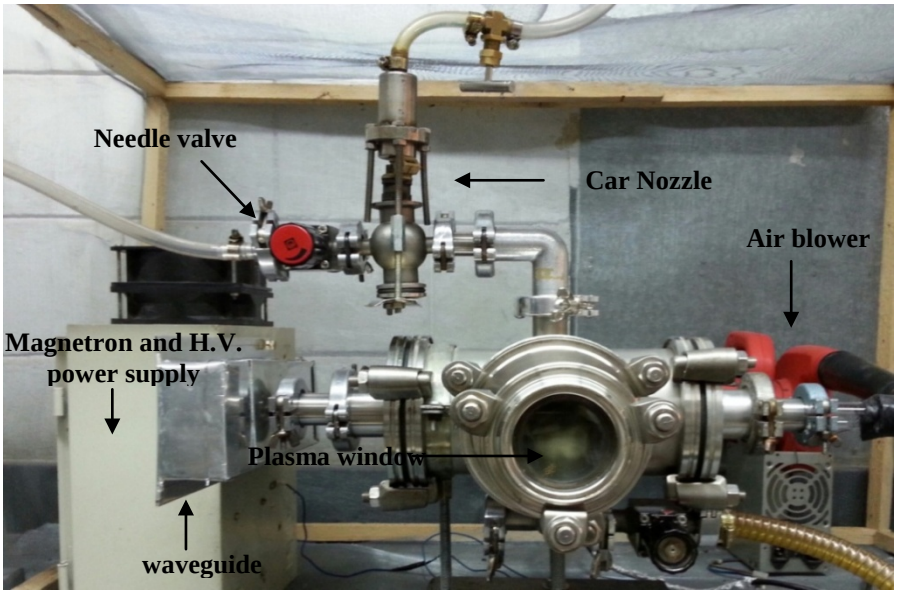


Fig.2 : Photograph of microwave induced plasma for nanocomposite thin films deposition.

Plasma parameters, electron temperature and density was measured using optical emission spectroscopy. Electron temperature was determined by two lines ratio method[8], the two spectral lines were (750.34, 811.5 nm), while the electron density was determined by Stark broading effect[9]. These measured values were T_e=0.51 eV and n_e=1.71x 10^{17} cm^{-3} The film thickness was measured using the optical interferometer method employing laser (532 nm), the films thickness t was determined using the formula [10].

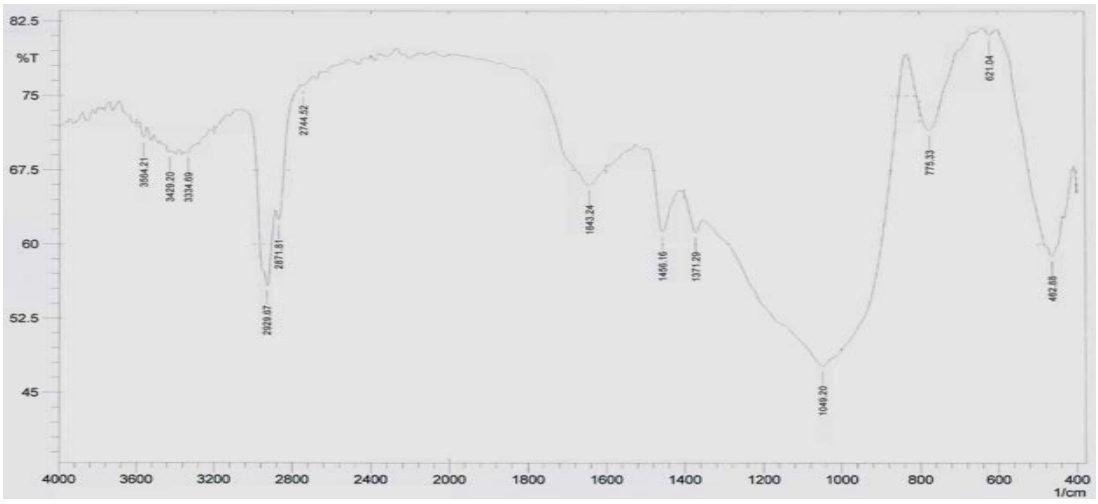
$$t = \frac{\lambda}{2} \cdot \frac{\Delta X}{X}$$

where Δx the width of the fringe, x the position of the fringe, and λ is the wavelength of the light. A double beam UV-VIS-NIR 210A Spectrometer was used to measure the absorption of polyaniline/silver thin films. The absorption data with films thickness can be used to calculate absorption coefficients of the films at different wavelengths which have been used to determine the energy band gap. FTIR spectra were recorded by using solid KBr discs and testing all samples by Shimadzu Co. FTIR 8000 series Fourier transform infrared spectrophotometer in the wavelength range 400-4000 cm^{-1}. The morphological surface analysis was carried out employing an atomic force microscope (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBS) from Angstrom Ad-Vance Inc.

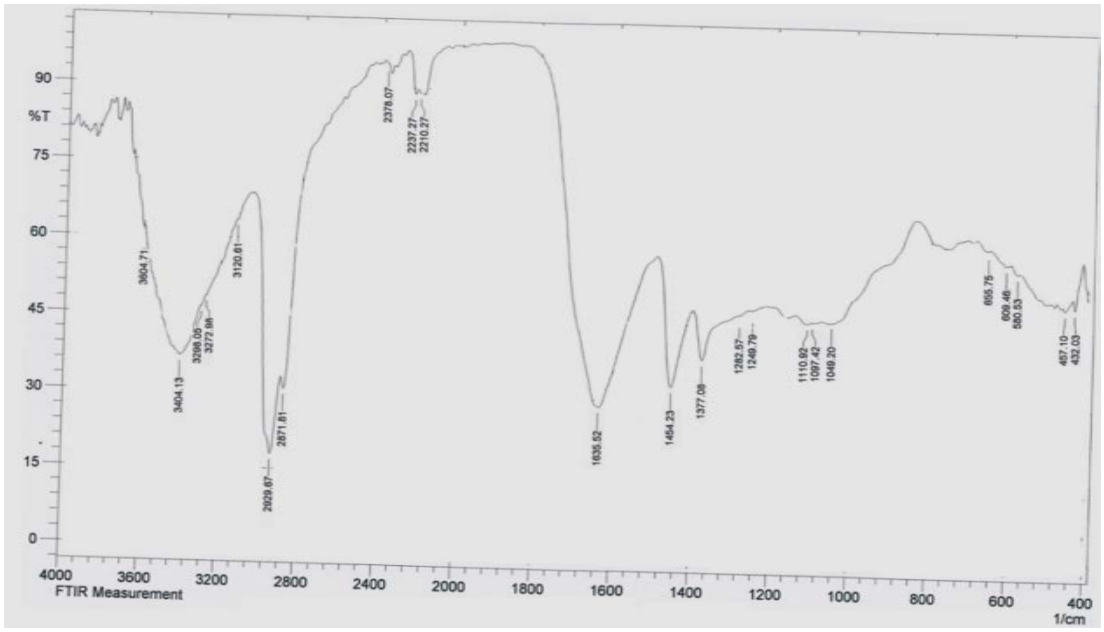
Results and discussion

FTIR analysis

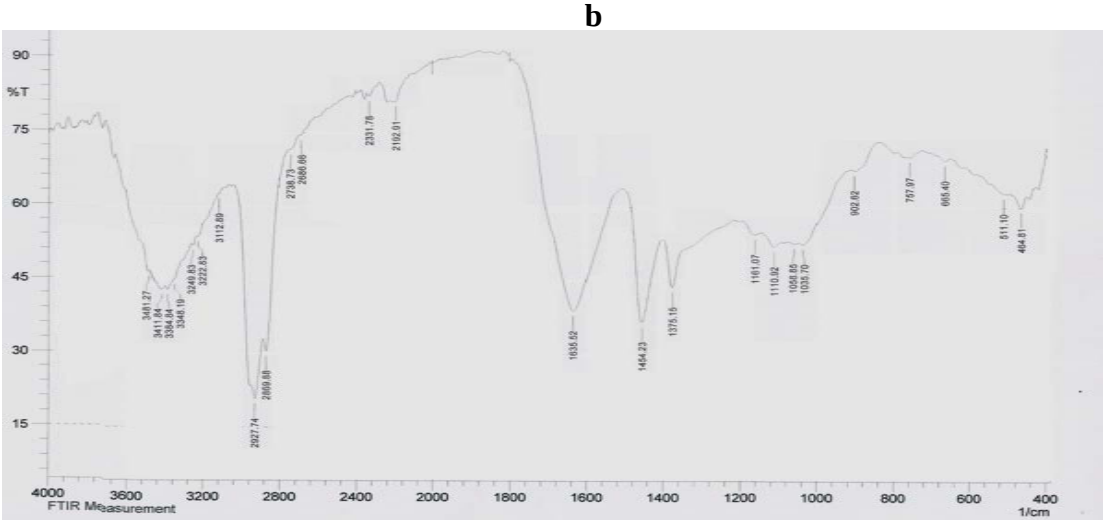
FTIR spectra of PANI and Ag/PANI nanocomposite is shown in Fig. 2. The band assignments of the FTIR absorption bands for pure aniline and different concentration of Ag/PANI is given in Fig.2 and Table 1. The bands related to N-H stretching of in aromatic amine appear at 3429cm^{-1}, 3411 cm^{-1} and 3404 $cm^{-1}$for PANI, Ag/PANI of 5% and 11%wt. of Ag respectively. The peaks at 2927 cm^{-1} and 2929 cm^{-1} is due to C-H stretch. The bands corresponding to quinoid (N=Q=N) and benzennoid (N-B-N) ring stretching modes were observed at 1635 cm^{-1}, 1643 cm^{-1} 1454 cm^{-1} and 1456 cm^{-1} respectively. Another characteristic band in the FTIR to C-N at about 1249 cm^{-1}, and for C-H bending vibration in the reign 1161cm^{-1}. The silver peaks appear at 757 cm^{-1} and 775 cm^{-1}.



a



b



c

Fig.3 :FTIR spectra a- polyaniline b- Ag/PANI nanocomposite with 5%wt. Ag c- Ag/PANI nanocomposite with 11%wt. Ag.

It is clear from Table 1 that there is a shift in the N-H stretching and C-N stretching band in the silver/Polyaniline nanocomposite thin films. This shift is an indication that silver nanoparticles cause a modification in the structure of the plasma polymerized aniline samples.

Table 1: FTIR common band for pure Polyaniline and different concentrations of Ag nanoparticles in PANI.

Bond range (cm^{-1})	Polyaniline	5%wt. silver/Polyaniline nanocomposite	11%wt. silver/Polyaniline nanocomposite	Expected vibration
3100-3500	3429	3411	3404	N-H stretching
2923-3017	2927	2929	2929	C-H stretching of aromatic ring
1500-1600	1635	1635	1643	C=C stretching of quinoid ring (N=Q=N)
1400-1480	1454	1454	1456	C=C stretching vibration of benzennoid ring (N-B-N)
1200-1300		1249		C-N stretching of primary aromatic amines
1100	1161	1161		C-H bending vibration
		757	775	Ag

The optical band gap (E_g)

The plot of $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ (where α is the absorption coefficient of films, h blank constant and υ frequency)for Ag/PANI nanocomposite thin films at different distances from the axis of the cylindrical plasma chamber (4.4, 4.0, 3.6, 3.4 cm), the corresponding film thickness at each distance were (133, 114, 110, 160 nm) respectively, is shown in the Fig. 4. The tested films has concentration of 5%wt Ag with aniline for the four distances. It is seen from Fig. 4 the change in the energy gap E_g from 3.6 to 3.2 eV. It is clear when the number of silver nanoparticles increase, the band gap E_g decrease.

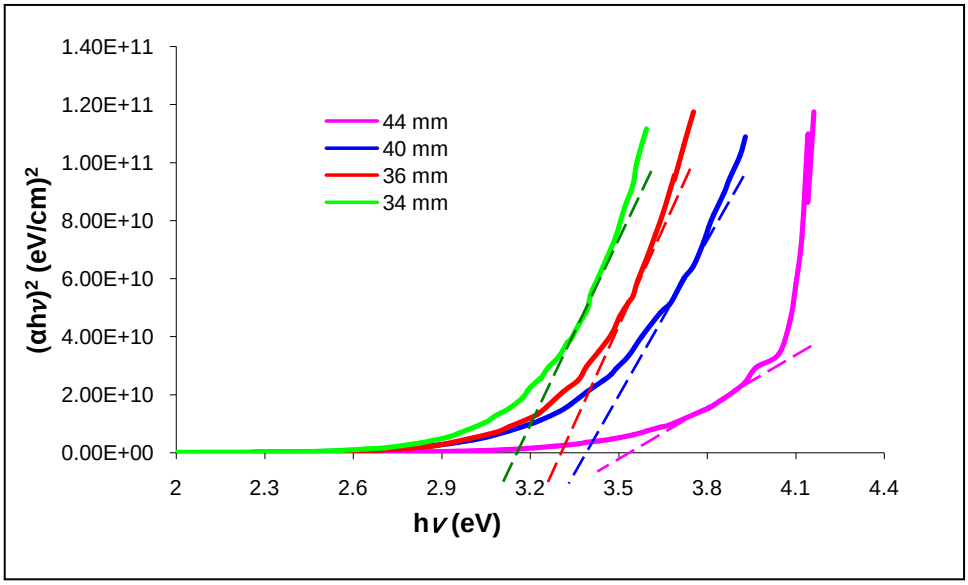


Fig. 4: Variation of $(\alpha h\upsilon)^2$ with photon energy $(h\upsilon)$ of the Ag/PAIN nanocomposite thin films at difference distances.

Fig.5 shows the $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ for Ag/PANI thin films with different concentrations deposited at the same distance (34 mm) from the quartz tube axis as shown in Fig. 5.

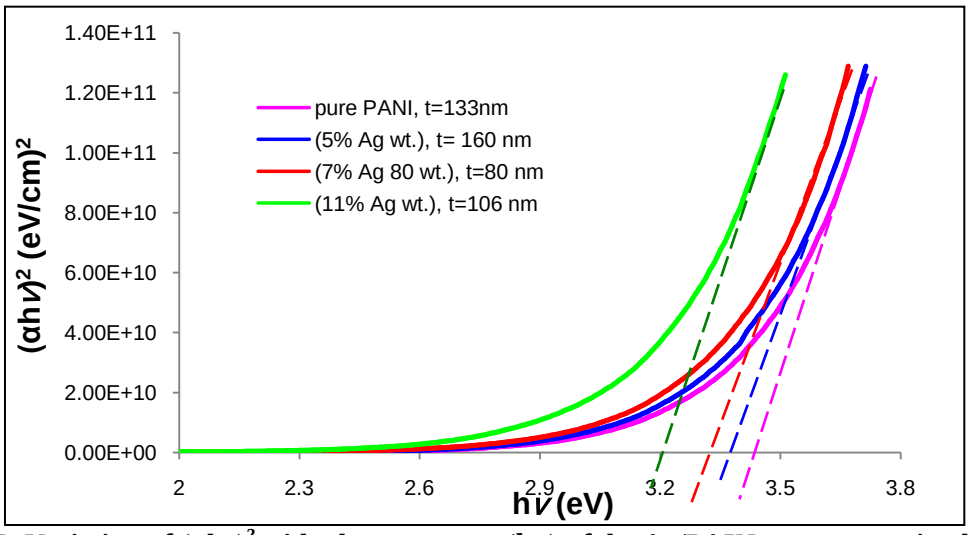


Fig.5: Variation of $(\alpha h\upsilon)^2$ with photon energy $(h\upsilon)$ of the Ag/PAIN nanocomposite thin films of different concentrations.

Atomic force microscopy (AFM)

The morphological characteristics of the pure polyaniline and Ag/PANI of 11%wt. Ag thin films have been studied by atomic force microscopy (AFM). The average surface roughness of the pure polyaniline film is 2.45 nm and the average diameter is 100.78 nm and for Ag/PANI film the average roughness is 6.25 nm while the average diameter is 115.10 nm.

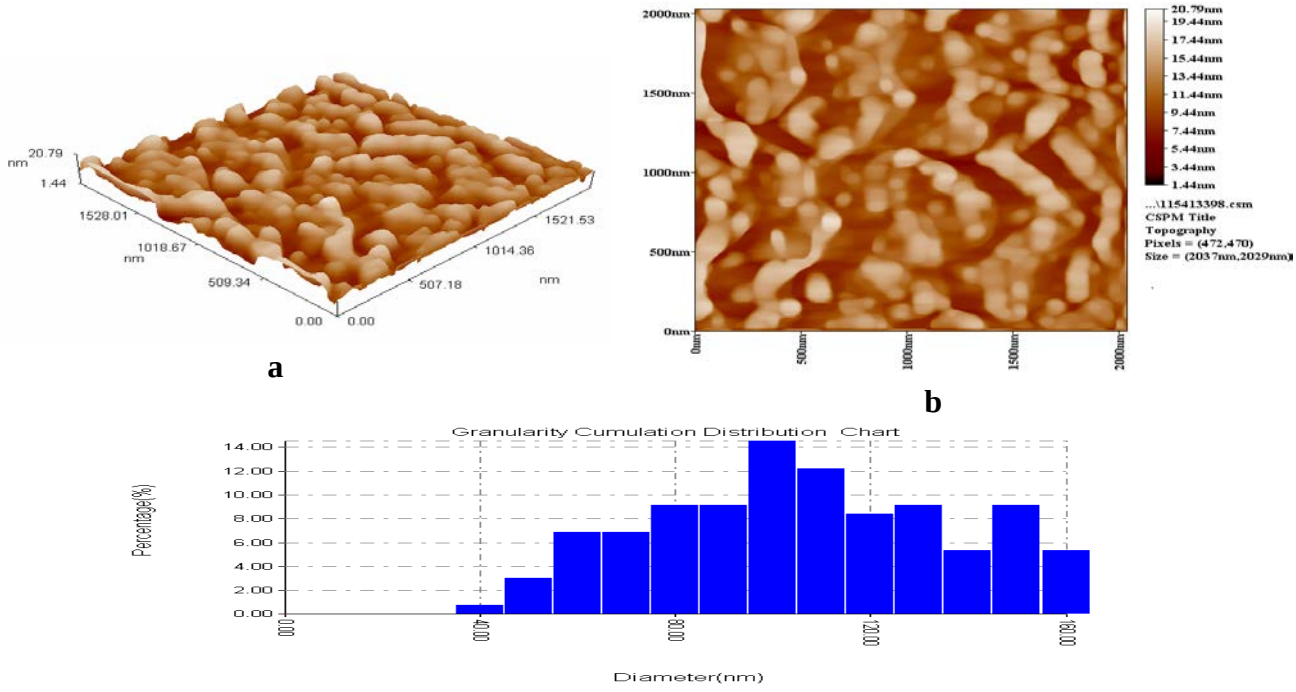
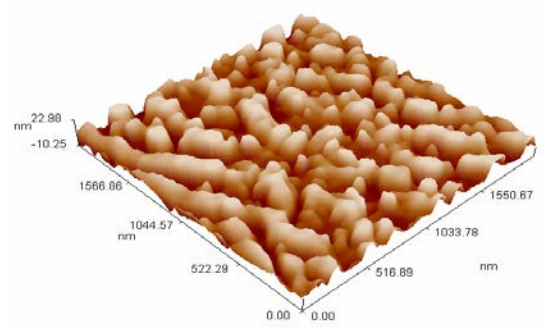


Fig.6: AFM photographs of pure polyaniline thin film surface a-3D image b-2 D image and c-size value distribution.



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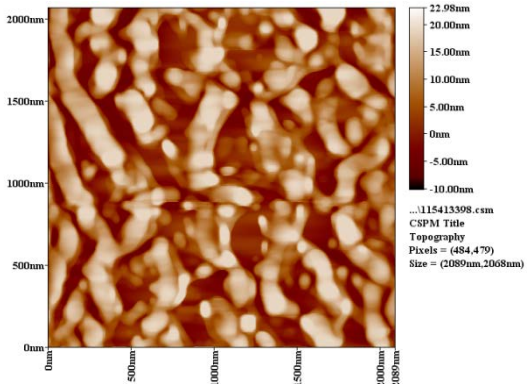

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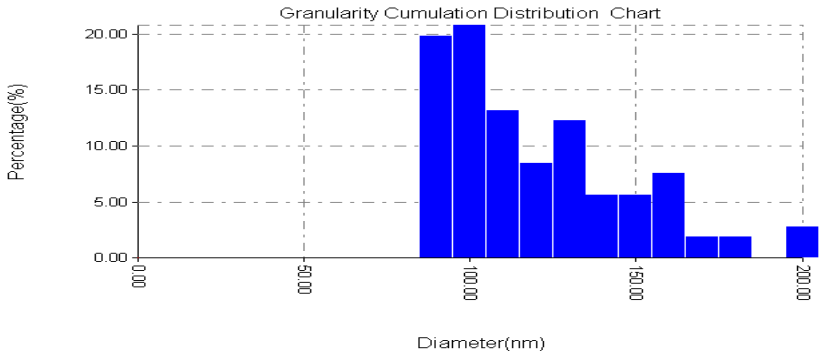


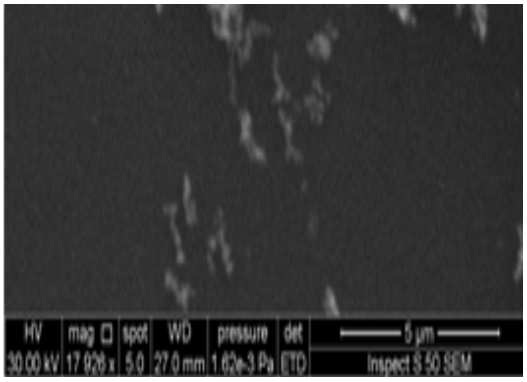
c

Fig.7: AFM photographs of 11% Ag in PANI/Ag thin film surface a- 3D image b-2 D image and c-size value distribution of PAIN/Ag.

Scanning electron microscopy (SEM)

The SEM images of the nanocomposite thin films of Ag/PANI is shown in Fig.8 a and b, respectively. As can be seen in this figure the Ag nanoparticles attached with polyaniline during polymerization.

The SEM images of composite show that there is few clusters of Ag particles in PANI matrix and there are uniform distribution of the Ag nanoparticles in the PANI matrix.



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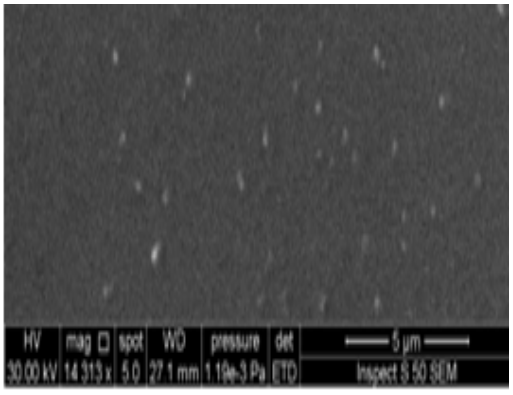

b

Fig.8: SEM image of a- 5%wt. and b- 11%wt. Ag with PAIN thin films.

Conclusions

PANI and Ag/PANI nanocomposite thin films with controlled optical energy band gap was successfully prepared by microwave induced plasma polymerization. Optical energy gap of these semiconductor films decreased with increasing concentrations of Ag nanoparticles. FTIR show the bonds of polyaniline and silver.AFM and SEM surface images show that the silver nanoparticle impeded inside the polyaniline matrices with uniform distribution.

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